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[Authors alone are responsible for all opinions expressed in their Communications.]

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No. 12.

STUDIES ON UREIDES. PART I. PREPARATION AND HYDROLYSIS OF DIACYL UREAS FROM ALIPHATIC ACIDS.

By A. E. A. WERNER.

[Read May 25. Published separately July 1, 1943.]

The symmetrical diacyl derivatives of urea are usually represented by the normal carbamidic NN′ structure in which both acyl groups are attached to nitrogen atoms; but E. A. Werner (1) has suggested that the second acyl group introduced into the molecule is attached to oxygen to form a pseudo-ureido ester, basing this structure on the behaviour of diacetyl urea when heated and when subjected to aqueous hydrolysis. These two possible structures may be represented by the following formulae A and B :—

(A) $O = C\begin{matrix}\diagup NH - CO - R \\ \diagdown NH - CO - R\end{matrix}$ (B) $HN = C\begin{matrix}\diagup NH - CO - R \\ \diagdown O - CO - R\end{matrix}$

The present communication is concerned with the preparation of diacyl ureas, containing two different acid radicals, since the properties of such compounds, in particular their behaviour on hydrolysis, may be expected to provide the necessary experimental evidence to distinguish conclusively between the two alternatives. If structure B correctly represents the diacyl ureas, then it ought to be possible to obtain two isomeric derivatives, namely:

(B_1) $HN = C\begin{matrix}\diagup NHCOR \\ \diagdown O - COR_1\end{matrix}$ and (B_2) $HN = C\begin{matrix}\diagup NH - CO - R_1 \\ \diagdown O - CO - R\end{matrix}$

depending upon the order in which the acyl groups are introduced into the molecule; whereas structure (A) can only yield one compound independent of the order in which the acyl groups are introduced. Three such pairs of diacyl ureas, namely, acetyl-propionyl, propionyl-butyryl, and acetyl-butyryl ureas, were prepared as described in the experimental part, but in no case was there any evidence of the existence of isomeric derivatives; thus, for example, the same substance is obtained by reacting monoacetyl urea with propionic anhydride or by reacting propionyl urea with acetic anhydride.

It would therefore seem as if diacyl ureas must have the symmetrical carbimidic NN′ structure (A), a fact which would be in agreement with the preparation of diacetyl urea by the interaction of phosgene with acetamide as described by Schmidt (2).

E. A. Werner (*loc. cit.*) has shown that, whereas monoacetyl urea undergoes no appreciable amount of hydrolysis when its aqueous solution is boiled

under reflux, the diacetyl derivative readily splits off one acetyl group. On the basis of the pseudo-ureido ester structure for the diacetyl derivative this hydrolysis was represented by the following equation :—

$$HN=C\begin{matrix}NH-CO-CH_3\\O-CO-CH_3\end{matrix} + H_2O == HN=C\begin{matrix}NH-CO-CH_3\\OH\end{matrix} + CH_3COOH, \quad (1)$$

since the resulting monoacetyl urea was stable towards mere aqueous hydrolysis. Upon investigating the behaviour towards aqueous hydrolysis of the other diacyl derivatives described in the present communication, it was found in all cases that, whereas the diacyl derivatives readily split off one acyl group, the monoacyl derivatives were resistant to aqueous hydrolysis. The extent of hydrolysis was followed by refluxing decimolecular solutions and titrating the liberated acid after specified intervals of time; the results so obtained are collected together in Table I.

TABLE I.—*Aqueous Hydrolysis of Diacyl Ureas.*

Nature of Acyl groups.	Percentage Hydrolysis after:				
	1 hour.	2 hours.	3 hours.	6 hours.	9 hours.
Diacetyl	21	32	45	71	86
Acetyl Propionyl ...	18	30	42	68	82
Dipropionyl ...	20	32	44	70	85
Propionyl Butyryl ...	15	24	35	65	80
Acetyl Butyryl ...	22	28	39	69	85
Dibutyryl ...	10	21	30	61	75

The course of the hydrolysis cannot, however, be represented by the above equation, because the product obtained by hydrolysis of those diacyl derivatives containing two different acyl groups was not homogeneous; the two acyl groups were eliminated simultaneously, so that the product of the reaction was an approximately equimolecular mixture of the two possible monoacyl derivatives. Assuming the NN′ carbamidic structure for the diacyl derivatives the course of the hydrolysis is best represented by the following equation :—

$$2\,O=C\begin{matrix}NH-CO-R\\NH-CO-R_1\end{matrix} + 2\,H_2O == O=C\begin{matrix}NH-CO-R\\NH_2\end{matrix} + O=C\begin{matrix}NH-CO-R_1\\NH_2\end{matrix} + R-COOH + R_1COOH \quad (2)$$

The stability of the monoacyl ureas towards aqueous hydrolysis was also confirmed by the fact that no urea is produced during the hydrolysis.

The hydrolysis of the diacyl and monoacyl ureas under alkaline conditions was next studied. It was found that both the diacyl and monoacyl derivatives were rapidly hydrolysed in the cold, the rate of hydrolysis being much greater

than in the case of aqueous hydrolysis. The actual results obtained in this series of experiments are collected in Table II.

TABLE II.—*Alkaline Hydrolysis of Di- and Mono-Acyl Ureas.*

Nature of Acyl groups.	Percentage Hydrolysis after: 5 mins.	10 mins.	20 mins.	30 mins.	60 mins	120 mins.
Diacetyl ...	23	33	48	55	67	75
Acetyl Propionyl ...	25	37	49	57	68	78
Dipropionyl ...	27	40	54	60	65	78
Propionyl Butyryl ...	25	36	49	58	64	74
Acetyl Butyryl ...	24	34	46	56	65	76
Dibutyryl ...	22	32	48	55	65	77
Acetyl ...	17	34	42	57	—	71
Propionyl ...	19	38	49	56	63	—
Butyryl ...	21	37	49	58	65	—

The monoacyl ureas were hydrolysed using one molecular proportion of sodium hydroxide, but in the case of the diacyl ureas two molecular proportions of alkali were used so as to cause complete hydrolysis. In the latter case the presence of free urea in the solution was tested for at frequent intervals, but the presence of urea was not detected until at least 50 per cent. hydrolysis had occurred, i.e. until the diacyl derivative had been completely converted into the monoacyl derivative. This observation confirms the fact that the diacyl ureas are more susceptible to hydrolysis than the monoacyl derivatives, and secondly that the hydrolysis proceeds in an asymmetrical manner as indicated in equation 2. The two acyl groups are not simultaneously removed with the immediate formation of urea from the diacyl derivative as would be represented by the following equation 3:—

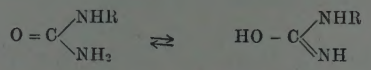
$$O=C\begin{matrix}NH-CO-R\\NH-CO-R_1\end{matrix} + 2H_2O = O=C\begin{matrix}NH_2\\NH_2\end{matrix} + R-COOH + R_1-COOH \qquad (3)$$

Since equation 1, involving the pseudo-ureido ester structure for the diacyl derivatives, does not correctly represent the course of the hydrolysis in aqueous solution, some alternative explanation must be sought to account for this remarkable difference between the behaviour of mono- and di-acyl derivatives towards hydrolysis, a difference which is not to be expected by a comparison of the normal structures, namely,

$$O=C\begin{matrix}NH-CO-R\\NH_2\end{matrix} \quad \text{and} \quad O=C\begin{matrix}NH-CO-R\\NH-CO-R\end{matrix}.$$

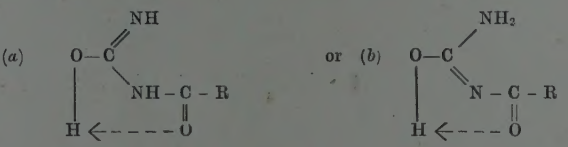
The following suggestions offer a possible explanation of the experimental observations. E. A. Werner (3) has shown that monosubstituted alkyl

derivatives of urea exist as an equilibrium mixture

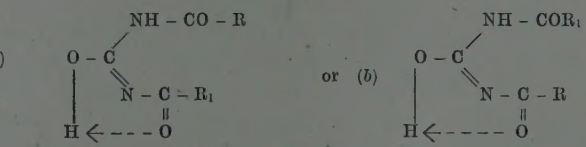


in which the relative amounts of the keto and enol tautomeric forms can be determined by the action of nitrous acid, e.g. in the case of methyl urea there is present 90 per cent. of the enol form. It is therefore probable that the acyl derivatives also exist as similar equilibrium mixtures in which the enol form will predominate to a large extent. Furthermore, the enol form will be stabilised owing to the formation of a six-atom cyclic structure due to chelation between the enolic hydrogen atom and the oxygen atom of the carbonyl group. The following equilibrium systems thus arise :—

(i) for the monoureides



(ii) for the diureides (with different acyl groups attached to the nitrogen atoms)



The formation of these stable chelate rings immobilises the active carbonyl group, thus preventing the removal of an acyl group by aqueous hydrolysis; in alkaline solution the chelate rings are destroyed prior to hydrolysis. It therefore follows that the monoacyl derivatives of urea will resist aqueous hydrolysis, but will be hydrolysed in alkaline solution; whereas in the case of the diacyl derivatives chelation can only immobilise one of the two acyl groups, so that the other acyl group is removed by aqueous hydrolysis. If there is no great difference in the character of the two acyl groups present in the molecule both will undergo enolisation and chelation to about the same extent, with the result that aqueous hydrolysis splits off both acyl groups in approximately equal amounts. This is the case with the diacyl derivatives in the present communication. The preparation and hydrolysis of mixed aliphatic aromatic diureides will be considered in a future communication.

Experimental.

Monoacyl derivatives of urea.—One molecular proportion of urea was added to one molecular proportion of the appropriate acid anhydride, containing concentrated sulphuric acid (0·5 c.c.), and a sufficient volume of the appropriate

fatty acid was subsequently added to effect complete solution. Brisk reaction started when the solution was warmed on the water-bath to a temperature ranging from 60° to 80° C., which was controlled by periodic immersion of the reaction flask in crushed ice. In order to avoid undesired side reactions accompanying the decomposition of the acetylated ureas, it is imperative that the temperature should not exceed 100° C. On completion of the reaction the solution was poured into cold water; the desired monoacyl derivatives were precipitated as white solids, which were filtered off and washed with 10 per cent. sodium bicarbonate solution.

Propionyl Urea was recrystallised from hot alcohol. White feathery crystals. M.P., 202° C. Yield, 70 per cent. of the theoretical. (Found N = 24·00 per cent. $C_4H_8ON_2$ requires N = 24·14 per cent.)

Butyryl Urea was recrystallised from hot water. Fine acicular crystals. M.P., 170° C. Yield, 65 per cent. of the theoretical. (Found N = 21·60 per cent. $C_5H_{10}O_2N_2$ requires N = 21·54 per cent.)

Symmetrical diacyl derivatives of urea.—These were obtained by treating the monoacyl derivatives with the appropriate acid anhydride or acid chloride, the temperature being kept as low as possible. Higher yields were obtained when the monoureide with lower molecular weight was first prepared and treated with the acid anhydride of higher molecular weight.

Acetyl Propionyl Urea was recrystallised from 50 per cent. propionic acid. White microcrystalline powder. M.P., 113° C. Yields, 80 per cent. and 60 per cent. of the theoretical. (Found N = 17·55 per cent. $C_6H_{10}O_3N_2$ requires N = 17·70 per cent.)

Dipropionyl Urea was recrystallised from hot water. White pearly leaflets. M.P., 207° C. Yield, 75 per cent. of the theoretical. (Found N = 16·60 per cent. $C_7H_{12}O_3N_2$ requires N = 16·40 per cent.)

Acetyl Butyryl Urea was recrystallised from petroleum ether. Glistening plates. M.P., 82° C. Yields, 80 per cent. and 65 per cent. of the theoretical. (Found N = 16·50. $C_7H_{12}O_3N_2$ requires N = 16·40 per cent.)

Propionyl Butyryl Urea was recrystallised from a mxiture of ethyl alcohol and petroleum ether. White glistening plates. M.P., 97° C. Yields, 75 per cent. and 65 per cent. of the theoretical. (Found N = 14·90 per cent. $C_8H_{14}O_3N_2$ requires N = 15·05 per cent.)

Dibutyryl Urea was recrystallised from mixture of benzene and petroleum ether. Waxy leaflets. M.P., 92° C. Yield, 60 per cent. of the theoretical. (Found N = 13·95 per cent. $C_9H_{16}O_3N_2$ requires N = 14·00 per cent.)

Aqueous Hydrolysis of Diacyl Ureas.—Decimolecular solutions of the respective compounds were boiled under reflux. The amount of fatty acid set free during the hydrolysis is determined periodically by titrating the solution with N/10 sodium hydroxide. On cooling the solution after hydrolysis white crystalline deposits were obtained. These were identified by determining their M.P.'s and nitrogen contents. Tests for the presence of urea in the solution were carried out by the urease method, but all proved negative.

Dipropionyl Urea yielded a white crystalline product. M.P., 203° C., and N = 24·20.

Acetyl Propionyl Urea yielded a white crystalline product. M.P., 192°–196° C. N = 25·60 per cent., 26·00 per cent. Equimolecular mixture of acetyl and propionyl ureas melts at 192°–194° C. and requires N = 25·75 per cent.

Propionyl Butyryl Urea yielded a white crystalline product. M.P., 159°–165° C. N = 22·60 per cent. Equimolecular mixture of propionyl and butyryl ureas melts at 159°–164° C. and requires N = 22·84 per cent.

Dibutyryl Urea yielded a white crystalline product. M.P., 171° C., and N = 21·45 per cent.

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No. 13.

THE ACTION OF THIONYL CHLORIDE ON UREA AND URETHANE.

By E. A. WERNER and A. E. A. WERNER.

[Read May 25. Published separately July 1, 1943.]

Schroeter and Lewinski (1) have shown that thionyl chloride and urethane interact in accordance with the following equation, leading to the formation of ethyl allophanate as the main product of the reaction:—

$$2\,O=C\begin{matrix}NH_2\\OC_2H_5\end{matrix} + SOCl_2 \;==\; O=C\begin{matrix}NH_2\\NHCO-OC_2H_5\end{matrix} + SO_2 + HCl + C_2H_5Cl.$$

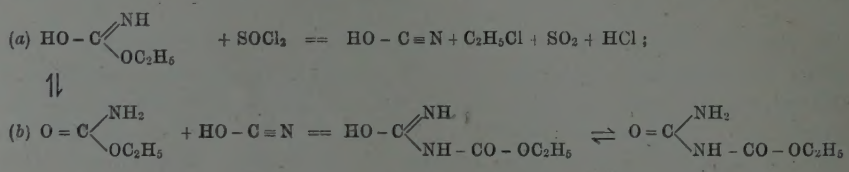
The reaction was carried out in benzene solution heated under reflux at 80° C. using two molecular proportions of urethane and one molecular proportion of thionyl chloride, and the yield of ethyl allophanate was 70 per cent. of the theoretical. This reaction was later investigated by Warren and Wilson (2), using a large excess of thionyl chloride in the absence of a solvent; they confirmed the formation of ethyl allophanate, but gave no reference to the yield obtained. The present authors find that the reaction proceeds rapidly without the use of either a solvent or an undue excess of thionyl chloride, and, as shown in the experimental part, the yield obtained under these simplified conditions is 90 per cent. of the theoretical, so that this reaction constitutes the best method for the preparation of ethyl allophanate. It has also been shown that sulphuryl chloride (3), phosgene (4), and phosphorus pentoxide (5) bring about a similar reaction, with the production of ethyl allophanate in varying amounts. The chief purpose of the present communication is to present a suitable mechanism to represent the course of these reactions supported by adequate experimental evidence.

Previous authors have simply represented the reaction as merely involving the removal of one molecule of ethyl alcohol from two molecules of urethane, without offering any explanation of the actual mechanism involved. Davis (6), in a communication on the hypothetical substance which he calls dicyanic acid,[1] represents the formation of ethyl allophanate from urethane as being due to the addition of this dicyanic acid to ethyl alcohol, according to the following equation:—

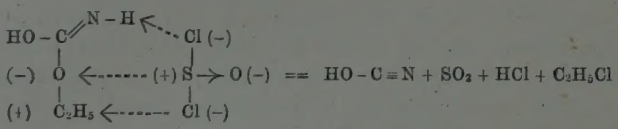
$$C_2H_5OH + H_2N-CO-N=C=O \;==\; O=C\begin{matrix}NH_2\\NH-CO-OC_2H_5\end{matrix}$$

[1] The existence of dicyanic acid must be regarded as very doubtful; the compound has never been isolated by Davis, and the reason adduced for its existence is based on a misjudged view of an analogy between cyanic acid and cyanamide. The latter forms the well-defined dimeride, dicyanodiamide, by mutual neutralisation of the *acidic* form $HN=C=NH$ and the *basic* tautomeric form $N\equiv C-NH_2$. Both tautomeric forms of cyanic acid are acidic, and therefore the formation of a dimeride is not to be expected.

Since the experimental conditions of the reaction under discussion would not be favourable to even the temporary formation of a substance so unstable as dicyanic acid, it is highly unlikely that this substance is concerned in the formation of ethyl allophanate. Accordingly it is suggested, in agreement with the view of one of us (E.A.W.) (7), regarding the structure of urethane in an acid medium, that in all these reactions the formation of the ethyl allophanate takes place in two stages. In the first stage cyanic acid is liberated in an "active" form (the exact nature of this "active" form of cyanic acid will be discussed in a later communication) from one molecule of urethane; in the second stage addition of "active" cyanic acid to a molecule of unchanged urethane occurs. This mechanism may be represented by the following equations:—



which proceed simultaneously once the initial decomposition of one urethane molecule has started. The actual manner in which the urethane molecule is attacked by the thionyl chloride may be satisfactorily represented by the following mechanism suggested by the work of Gerard (8) on the action of thionyl chloride on hydroxylic compounds:—



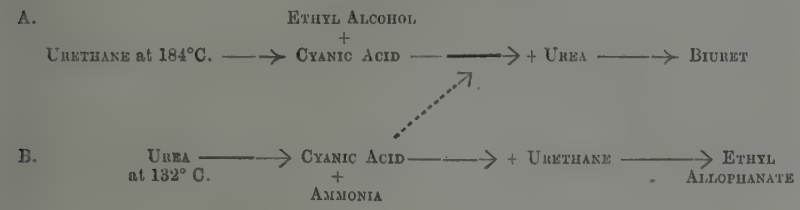
(the signs in parentheses represent the tendencies indicated).

The high yield of ethyl allophanate is due to the fact that reaction (*b*) proceeds more rapidly than reaction (*a*), so that there is always unchanged urethane present in the system, with which the cyanic acid can immediately combine before it polymerises with the formation of cyanuric acid.

The analogous reaction of thionyl chloride on urea has been studied by Warren and Wilson (*loc. cit.*), who claim as the chief product of the reaction the formation of biuret, which they represent as taking place by the elimination of one molecule of ammonia from two molecules of urea; they give no figures as to the actual yield obtained. A repetition of this experiment as shown in the experimental part has proved that in actual fact the yield of biuret is very small, being of the order of 10 per cent. of the theoretical; the main products of the reaction are ammonium chloride, ammonium cyanate, and other decomposition products of cyanic acid. If this reaction merely involved the removal of one molecule of ammonia from two molecules of urea one would

expect the yield of biuret to be considerably higher. It is evident that the reaction proceeds by a similar mechanism to that suggested in the case of urethane with, however, one important point of difference, namely, the fact that the urea molecule is broken down by the thionyl chloride at a much greater rate than that at which it combines with unchanged urea to form biuret; for this reason most of the cyanic acid enters into side reactions with a corresponding decrease in the yield of biuret. This difference between urethane and urea is what would be expected, since urea breaks up into ammonia and cyanic acid at the relatively low temperature of 132° C., whereas urethane only decomposes into ethyl alcohol and cyanic acid at 184° C.

This explanation of the marked difference in these two analogous reactions receives further support from a study of the action of thionyl chloride on an equimolecular mixture of urea and urethane. There are two alternative courses that the reaction may follow, represented schematically as follows:—



The relative yields of biuret and ethyl allophanate will indicate the extent to which the two reactions occur. It was found that the yield of ethyl allophanate was 85 per cent. of that required according to reaction scheme B, whereas the yield of biuret was only 10 per cent. of that required according to reaction scheme A. This result indicates clearly that the urea is preferentially decomposed to yield cyanic acid, which combines with the undecomposed urethane. This idea is also supported by the experimental observation that in this reaction no ethyl chloride is produced, whereas in the reaction with urethane alone ethyl chloride distils over in copious amount as soon as the reaction starts. This complete absence of ethyl chloride indicates furthermore that the small amount of biuret formed is not produced according to reaction mechanism A, but is formed as the result of cyanic acid produced in reaction mechanism B combining with some unchanged urea, as indicated above by dotted arrow.

A final point of practical importance is the fact that cyanuric acid can be produced in quantitative yield by heating ethyl allophanate just above its melting point; it decomposes smoothly in accordance with the following equation:—

$$3\ O=C\begin{matrix}NH_2\\ NHCO-OC_2H_5\end{matrix} \longrightarrow 2\ C_3H_3N_3O_3 + 3\ C_2H_5OH$$

Schroeter and Lewinski (*loc. cit.*) heated ethyl allophanate with thionyl chloride in a sealed tube at 140°–150° C. using xylene as a diluent, but only succeeded in obtaining a 60 per cent. yield of cyanuric acid. If, however, thionyl chloride is allowed to react with urethane at the elevated temperature of 200° C. cyanuric acid is produced directly in one stage in quantitative yield, and this reaction constitutes the most convenient method for the preparation of pure cyanuric acid, since its formation is not accompanied by any solid by-products.

Experimental.

Action of thionyl chloride on urethane.—Urethane (27 g.) was warmed with thionyl chloride (25 g.) to 60° C., when a vigorous reaction set in accompanied by the evolution of hydrochloric acid, sulphur dioxide, and *ethyl chloride,* which were absorbed in alcoholic potassium hydroxide. After 1½ hours heating the reaction is completed, and the residue is extracted with ether (40 c.c.) and filtered. Weight, 17·7 g. Recrystallised from hot water M.P. is 190° C. (Found N = 21·09 per cent. $C_4H_8N_2O_3$ requires N = 21·2 per cent.)

Action of thionyl chloride on urea.—Urea (20 g.) was warmed to 70° C. with thionyl chloride (25 g.). Reaction occurs with evolution of hydrochloric acid and sulphur dioxide absorbed in alcoholic potassium hydroxide. Residue is extracted with ether (50 c.c.). Yield of biuret obtained was 2 g.

Action of thionyl chloride on an equimolecular mixture of urethane and urea.—A finely powdered mixture of urethane (14 g.) and urea (9 g.) was warmed to 80° C. with thionyl chloride (25 g.). Reaction occurred with evolution of hydrochloric acid and sulphur dioxide. The solid residue was extracted with ether to remove unchanged urethane, and then with hot water to remove biuret. The residue was recrystallised from water. Weight, 8·5 g. M.P., 190° C. (Found N = 21·15 per cent.) The aqueous filtrate yielded 2·5 g. of biuret and 4 g. of ammonium chloride.

Thermal decomposition of ethyl allophanate.—Ethyl allophanate (13·2 g.) was heated to 200° C. for 45 minutes. Ethyl alcohol distilled over, and a residue of pure anhydrous cyanuric acid remained. Weight, 7·85 g., corresponding to 93·5 per cent. of the theoretical.

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No. 14.

REPORT OF THE IRISH RADIUM COMMITTEE FOR THE YEAR 1942.

There has been a considerable reduction in the demand for radon, only 1,109 tubes containing 6,648 millicuries having been issued, as compared with 1,400 containing 10,613 millicuries in 1941.

Mr. M. G. Kelliher was elected to the Radium Exhibition falling vacant during the year.

Returns from the chief users record the treatment of the following cases with radon or radium element:—

MALIGNANT CASES.

St. Anne's Hospital, Dublin	140
Dr. Oswald Murphy, St. Vincent's Hospital ...	80
Dr. Oliver Chance	14
Dr. d'Abreu, City & County Hospital, Waterford ...	10
	244

NON-MALIGNANT.

Dr. Murphy	67	
Dr. Chance	38	
Meath Hospital	2	
Dr. Solomons	1	
	108	Total: 352

The returns show that for the cases of malignant disease first seen during 1942 the numbers treated by the different methods were as follows:—

1.	Number of cases of all types of malignant disease seen during 1942 ...	928
2.	„ „ treated during 1942	730
3.	„ „ „ by Surgery alone	54
4.	„ „ „ by Radium or Radon alone ...	184
5.	„ „ „ by X-ray alone	406
6.	„ „ „ by Surgery and Radium ...	17
7.	„ „ „ by Surgery and X-rays ...	26
8.	„ „ „ by Radium and X-rays ...	41
9.	„ „ „ by Surgery, Radium, and X-rays	2

Dr. Oswald J. Murphy [St. Vincent's Hospital, Dublin] reported the treatment with radon of the following cases:—

Malignant.—Carcinoma of the ear, 2; lip, 5; cheek, 1; parotid, 1; tongue, 3; tonsil, 1; œsophagus, 1; uterine cervix, 8; uterine body, 2; skin, 31. Rodent Ulcers, 27. Total, 82.

Non-Malignant.—T.B. Peritonitis, 10. Uterine Hæmorrhage, 4. Angiomata, 18. Lupus Vulgaris, 2. Lupus Erythematosus, 2. Keloids, 2. Warts, 29. Total, 67.

Dr. Oliver Chance [Richmond, Sir Patrick Dun's, Dr. Steevens', Rotunda, and Coombe Hospitals] reported the treatment with X-rays, radium, or radon, of the following cases:—

Malignant.—Carcinoma of the skin, 13; lip, 12; tongue, 4; palate, 1; floor of mouth, 1; fauces, 2; pharynx, 3; extrinsic larynx, 4; post-cricoid, 1; breast, 17; cervix, 6; body of uterus, 1; ovary, 1; vulva, 2; prostate, 1; lung, 1; glands (unclassified), 3. Sarcoma, 1. Brain Tumour, 1. Rodent Ulcers, 37. Total, 112.

Non-Malignant.—Toxic Goitre, 12. T.B. Peritonitis, 6. Non-malignant uterine conditions, 4. Naevi, 8. Various other non-malignant conditions, 8. Total, 38.

Dr. Bethel Solomons reported the curing by radon treatment of a case of Metropathia Hæmorrhagica.

The Meath Hospital reported the treatment by radon of one case of Toxic Goitre, and one of Hyperthyroidism.

No. 15.

THE CHEMICAL CONSTITUENTS OF LICHENS FOUND IN IRELAND —*LECANORA GANGALEOIDES*.—PART 3.—THE CONSTITUTION OF GANGALEOIDIN.

BY V. E. DAVIDSON, PH.D., J. KEANE, PH.D.,

AND

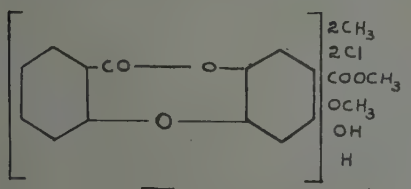
T. J. NOLAN, B.A., D.Sc.,
University College, Dublin.

INTRODUCTION.

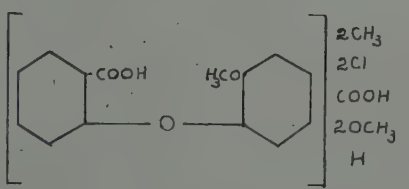
[Read MAY 25. Published separately AUGUST 13, 1943.]

NOLAN and Keane (Sci. Proc. R.D.S., 1935, **21**, p. 141; 1940, **22**, p. 199) have described the isolation from the lichen *Lecanora gangaleoides* of atranorin and chloratranorin, arabitol, rhodophyscin, endococcin (the latter transformed into the former by boiling with acetic acid), a chlorine-containing substance which they named gangaleoidin and to which they gave the formula $C_{18}H_{14}O_7Cl_2$, and another chlorine-containing substance of much higher melting point than gangaleoidin, differing from the latter in methoxyl content, but otherwise giving analyses identical with those of gangaleoidin.

Gangaleoidin was found to contain two methoxyl groups, a hydroxyl group, and a lactone group (CO–O). One of the methoxyl groups was considered to be present as a carboxylic ester, so that the formula was written $C_{14}H_7OCl_2(COO)(COOCH_3)(OCH_3)(OH)$. General considerations of this formula and lack of reactivity of the remaining oxygen atom indicated the presence of two aromatic rings joined by an oxygen bridge. Since the chlorine atoms were not affected by boiling alcoholic potash they could not be present in an aliphatic side chain, but must be substituents in a benzene ring. General considerations of lichen chemistry led Keane and Nolan to the view that the aliphatic side chains consisted of two methyl groups and not of a single ethyl substituent. Accordingly they wrote the formula for gangaleoidin as I; they attempted by means of pyrolytic methods to effect scission of the molecule but without success. When the dicarboxylic acid II

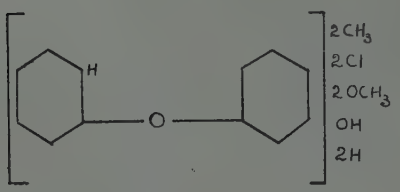


I

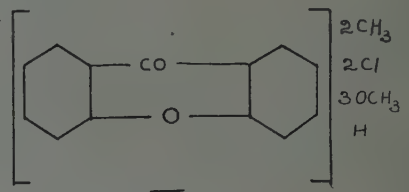


II

derived from gangaleoidin was distilled under reduced pressure three compounds were obtained. One was the monocarboxylic acid produced by partial decarboxylation; the second was a diphenyl ether of the constitution III, complete decarboxylation and partial demethylation having taken place; the third was a neutral product of formula $C_{18}H_{16}O_5Cl_2$, which contained three methoxyl groups. This product, though it did not form a salt with concentrated hydrochloric acid, is most probably a xanthone IV.

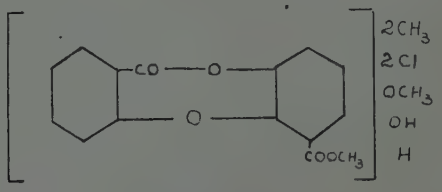


III



IV

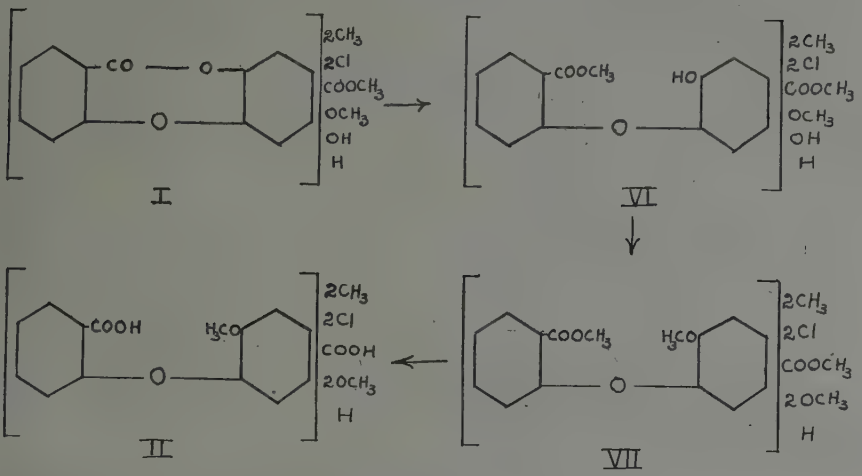
Should it have been formed without any preliminary isomerisation then the carboxylic ester group in gangaleoidin must be in the ortho position to the oxygen bridge as in V, or alternatively this ortho position must be unsubstituted.



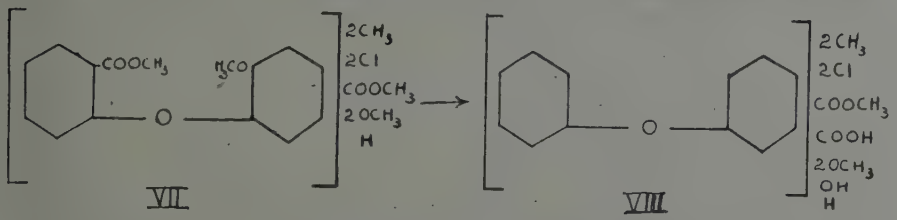
V

Attempts by Keane and Nolan (*loc. cit.*) to effect dechlorination or fission of gangaleoidin with hydriodic acid gave unworkable products.

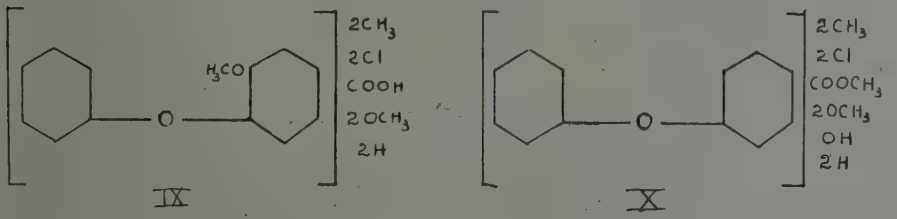
It will be noted from these earlier results that, with the exception of the position of the lactone bridge and the ether link, and a speculation as regards the position of the carboxylic ester group, no evidence was available regarding the positions of the various substituents in the benzene rings. Even the existence of two methyl substituents was inferred by analogy. In the present paper we have investigated further the constitution of gangaleoidin. A Kuhn-Roth determination established the presence of two C-methyl groups. Our experiments were next directed towards a re-examination of the dicarboxylic acid, referred to above, which was produced from gangaleoidin by the following series of reactions:—



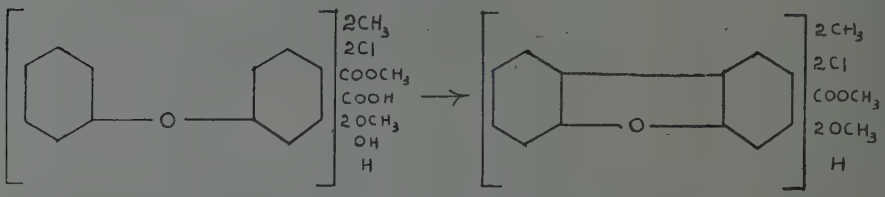
The three different substances obtained by distilling in vacuo the product II are in accordance with the dicarboxylic acid structure attributed to the latter; there are, however, certain factors which justify one in entertaining the view that the hydrolysis of VII may have proceeded in accordance with the scheme



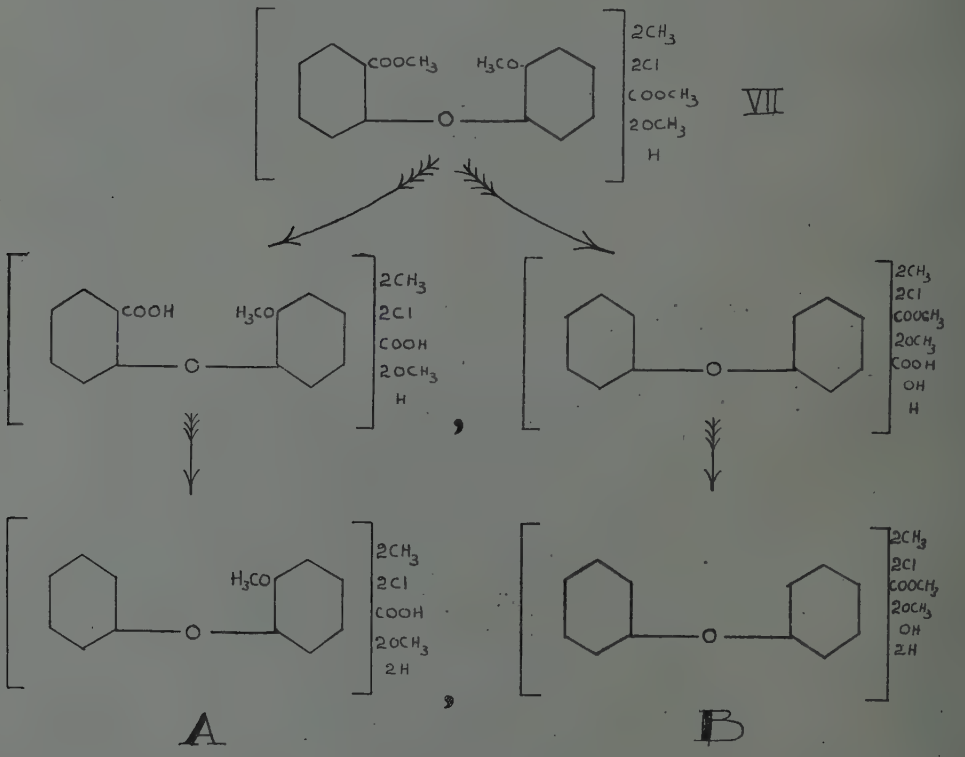
so that the product of hydrolysis instead of being a dicarboxylic acid may in fact be the phenol carboxylic acid carboxylic ester VIII. Thus, the dicarboxylic ester VI (*supra*), which contains free hydroxyl groups, on vigorous hydrolysis with alcoholic or aqueous potash loses only one methoxyl group (Keane and Nolan, *loc. cit.*). This would support the transformation VII → VIII. The easy demethylation of chlorinated phenol ethers is known (Calam and Oxford, J.C.S., 1939, p. 281). It would follow from the structures II and VIII that the product obtained by the loss of one molecule of carbon dioxide, which loss may be effected more readily by heating in anhydrous formic acid than by heating in vacuo, would have either of the formulae IX or X.



The insolubility of II (or VIII) in ligroin, and the solubility of the product obtained from it by decarboxylation, as well as the weak acidity of the latter, would favour the formula X for the latter. The only way, however, in which one could account for the loss of carbon dioxide and water from a substance of formula VIII would be a transformation of the type



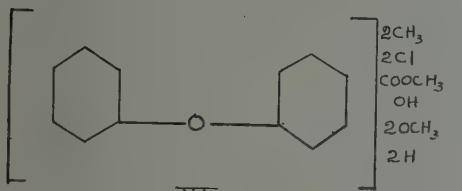
which would also explain the absence of salt formation with concentrated hydrochloric acid. It thus becomes a question of deciding whether the hydrolysis of VII followed by decarboxylation takes the course A or B.



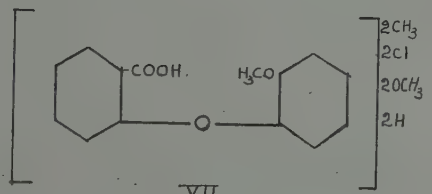
On treating the intermediate hydrolysis product with sulphuric acid and acetic anhydride the product is recovered unchanged. This favours the course A unless the hydroxyl group in the first stage of B is so acidic that it

does not readily acetylate. On the other hand, the final product obtained in the above series of reactions when treated with acetic anhydride and sulphuric acid does *not* acetylate, but loses a molecule of methyl alcohol, forming a lactone. This reaction is consistent with either of the courses A or B. However, if course B were correct, on treating the lactone with methyl alcoholic potash the original substance should be regenerated. In fact, a new isomer is obtained. Accordingly, the series of reactions is represented by course A, and hydrolysis of VII produces a dicarboxylic acid from which a monocarboxylic acid is produced by partial decarboxylation. It is peculiar that the dicarboxylic acid is unaffected by acetic anhydride and sulphuric acid, while the monocarboxylic acid forms a lactone. It is also worthy of note that methylation of the hydroxyl groups in gangaleoidin methyl ester facilitates the hydrolysis of *both* carboxylic ester groups, while in the case of the unmethylated product only *one* carboxylic ester group is hydrolysed.

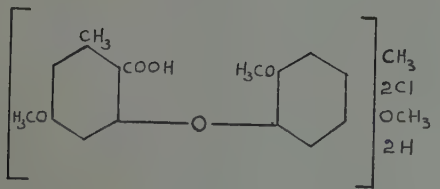
Whereas the monocarboxylic acid produced in the series of reactions A is readily methylated by diazomethane to an ester m.p. 78–79° C., the isometric compound which must have the structure XI



XI



XII



XIII

is not methylated under these conditions, nor is it readily extracted from ether solution with dilute sodium hydroxide. On the other hand, it is methylated in boiling acetone by dimethyl sulphate and potassium carbonate to the compound m.p. 78–79° C., referred to above.

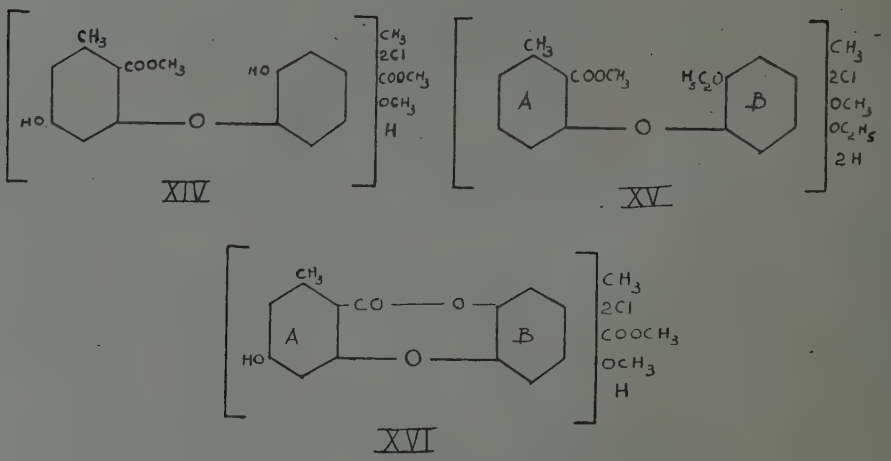
From the fact that the monocarboxylic acid undergoes ring closure with the elimination of methyl alcohol it must have the structure XII.

Further information with regard to its structure was obtained by treating its ester in carbon tetrachloride solution with chlorine followed by reduction with stannous chloride; 4·6 dichlor methyl orsellinate 5 methyl ether was isolated

from the products of reaction. It thus follows that the monoacid has the structure XIII.

An attempt was next made to gain insight into the structure of gangaleoidin itself. The action of chlorine, followed by reduction with stannous chloride, on gangaleoidin methyl ester gave 4·6 dichlor methyl orsellinate. Gangaleoidin methyl ester must accordingly have the structure XIV.

It is most unlikely that the series of reactions would have involved demethylation, as such did not occur in the case of similar experiments carried out to elucidate the structure of the monoacid. To confirm this, gangaleoidin methyl ester was ethylated with diazoethane, and by subsequent hydrolysis, decarboxylation, and methylation, the substance XV was formed. Chlorination followed by reduction yielded 4·6 dichlor methyl orsellinate 5-ethyl ether, thus confirming the presence of a hydroxyl group in ring A. Thus, gangaleoidin must have the structure XVI.

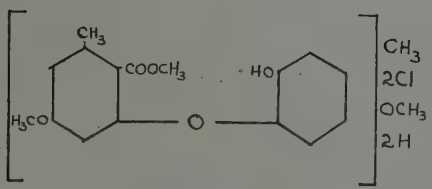


Obviously the second CH_3 group and the OCH_3 group must be in ring B. The establishing of the position of the hydroxyl group in ring A precludes the existence in gangaleoidin itself of a carboxylic ester group in ring A, because it would have to be ortho to the hydroxyl group, and such a system would give a positive reaction with ferric chloride. Gangaleoidin, however, does not give such a reaction, hence the ester group must be in ring B. Consequently there are in ring B methyl, methoxyl, and ester substituents, leaving only one possible position vacant, which must be occupied by either hydrogen or chlorine; thus there must be at least one chlorine atom in ring A.

With regard to the determination of the position of the ester group in ring B, a reaction using 2·6 dichlorquinone-chlorimide has been employed.

This reagent has been shown by Gibbs (J. Biol. Chem., 1927, **72**, p. 649), Theriault (Ind. & Eng. Chem., 1929, **21**, p. 343), and Todd (J.C.S., 1940, p. 1208) to give a blue colour in a sodium borate buffer (pH 9·2) with substances containing a hydroxyl group para to hydrogen, the reaction being essentially the formation of an indophenol. Our experiments indicate that the reaction also takes place if the position para to the hydroxyl is occupied by a COOH group or by a chlorine atom, but *not* if an ester group is present in the para position. The blue colour is modified by substituents, more particularly by the presence of other hydroxyl groups. The reaction resembles the known coupling of a diazonium salt with a p-hydroxy carboxylic acid with elimination of carbon dioxide.

Now gangaleoidin methyl ester XIV does not give an indophenol reaction, whereas the derivative XVII



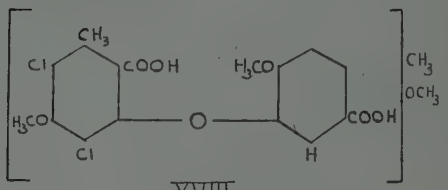
XVII

in which the ester group has been eliminated from ring B gives a bright blue colour. This is evidence that, in the case of gangaleoidin methyl ester, the ester group in ring B must be present in a position para to hydroxyl. Since the dicarboxylic acid II apparently forms a xanthone on distillation in vacuo, the position ortho to the oxygen bridge in ring B must contain hydrogen. Thus, in the case of gangaleoidin, there are in ring B, in addition to the lactone and oxygen bridges, methyl, methoxyl, ester, and hydrogen, so that the two chlorine atoms must be in ring A. This conclusion has been confirmed by a repetition of the thermal decomposition experiments of Keane and Nolan (Sci. Proc. R.D.S., **22**, 1940, p. 206) with gangaleoidin methyl ester, in which, in addition to the production of an isomer of gangaleoidin methyl ester, we also obtained a small amount of 4·6 dichlor orsellinic ester.

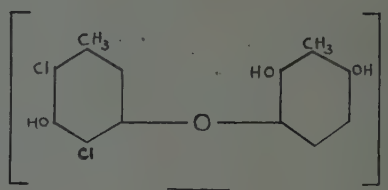
In order to fix the position of the methoxyl group in ring B gangaleoidin was demethylated in acetic acid solution, with hydrobromic acid in the presence of red phosphorus. The product obtained had the constitution $C_{14}H_{12}O_4Cl_2$, and on methylation gave the same product, m.p. 165° C., as was obtained by Keane and Nolan (*loc. cit.*) by the pyrolysis of the dicarboxylic acid II (*supra*), which acid we can now express by the formula XVIII.

The substance of constitution $C_{14}H_{12}O_4Cl_2$ gave a red coloration with bleaching powder, and accordingly must contain two hydroxyl groups meta to

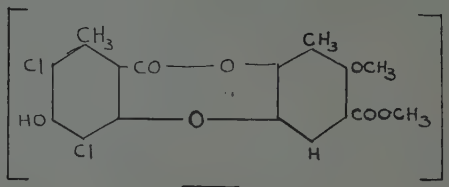
each other. Thus it must have the constitution XIX; so that XX must be the structure of gangaleoidin.



XVIII

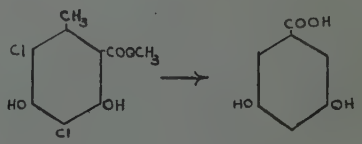


XIX



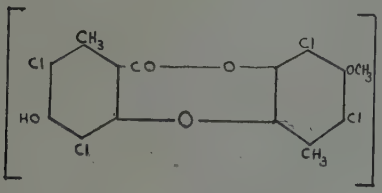
XX

It was thought that a potash fusion of gangaleoidin methyl ester should give confirmatory evidence of the orientation of the substituents in the B ring of gangaleoidin, as the replacement of the chlorine atoms of the A ring by hydroxyl during fusion should result in the eventual destruction of that ring, leaving the residue of the B ring. However, potash fusion of gangaleoidin methyl ester gave a product of formula $C_{14}H_{12}O_6$. This substance contains one carboxylic acid group, four hydroxyls, and probably one methyl group. It gives a blood-red coloration with bleaching powder, indicating the presence of hydroxyls meta to each other, and no ferric chloride reaction, showing that the carboxylic acid group is not ortho to hydroxyl. Owing to the large loss of material in the fusion it was not possible to investigate the constitution of the product in the desirable detail, but a potash fusion of 4·6 dichlor orsellinic ester gave a possible clue to its structure. It has been found that dichlor orsellinic ester on potash fusion gives α-resorcylic acid

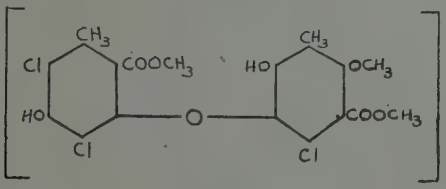


the chlorine atoms not being replaced by hydroxyls in the process as would be expected. Incidentally, a good yield of α-resorcylic acid was obtained by a

potash fusion of diploicin, which one of us (T.J.N.) believes to have the constitution



Thus gangaleoidin in the process of potash fusion apparently undergoes an intramolecular rearrangement accompanied by oxidation, resulting in the production of a tetrahydroxy diphenyl carboxylic acid derivative, made up of the two units, α-resorcylic acid and 2·6 dihydroxytoluene. Any question of the possible existence in gangaleoidin of a diphenyl structure with a non-reactive hydroxyl group is, apart from other considerations, excluded by the fact that gangaleoidin methyl ester can be chlorinated to a monochlor derivative in which the chlorine has entered the B ring. This derivative, on the above considerations, would have the constitution



It can be converted to a dimethyl ether, which, in turn, can be hydrolysed to a dicarboxylic acid which resists even partial decarboxylation owing to the steric effect of the ortho chlorine atom.

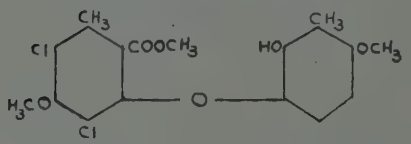
EXPERIMENTAL.

Reactions of 2 : 6 Dichlorquinone Chlorimide with various Oxy-compounds.

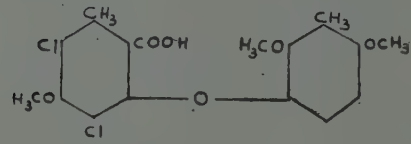
2 : 6 dichlorquinone chlorimide was prepared according to the method of Kollrepp (A. 234·18). The reagent was used in the presence of a sodium borate buffer (Palitzsch, J. Biol. Chem., 1927, **72**, 651). A small quantity of the substance under test was taken in a test tube and to it was added about 10 c.c. of the solution of the sodium borate buffer (pH 9·2), a small amount of alcohol being added in the case of substances soluble with great difficulty; there

was then added a drop or two of a suspension of the quinonechlorimide in water. The colour developed rapidly in most cases.

Substance.	Colour.	Reaction.
Phenol	Pure Blue	+
Catechol	Bluish purple	+
Resorcinol	Violet red	+
Orcinol	Reddish Purple	+
p-chlorphenol	Intense Blue	+
p-hydroxy Benzoic acid	Deep blue	+
p-hydroxy Benzoic ester	Olive brown	—
Gangaleoidin	Olive brown	—
Gangaleoidin Methyl ester	Steel colour	—
Gangaleoidin chlor-methyl ester	Slate grey	—
Diploicin	Olive brown	—
Diploicin Methyl ester	Intense blue	+
4·6 dichlor Methyl orsellinate	Violet purple	+



... ... Blue +



... ... Olive brown —

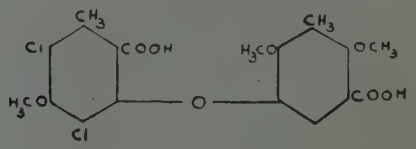
Kuhn-Roth Estimation of C-Methyl in Gangaleoidin.

7·520 mg. ... ... 4·25 c.c. N/100 NaOH.

Found C-Methyl = 8·5 %.

$(CH_3)_2C_{16}H_8O_7Cl_2$ requires C-Methyl = 7·2 %.

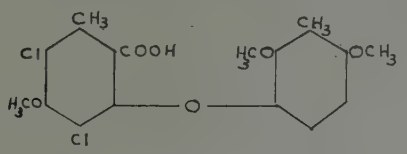
Attempted Acetylation of the Dicarboxylic Acid.



0·05 g. of dicarboxylic acid, m.p. 216–217° C., was dissolved in 3 c.c. acetic anhydride, and a few drops of sulphuric acid added. The light straw-coloured solution was allowed to stand for two hours. It was then poured into 10 c.c.

water, and after standing a further two hours the precipitate was filtered off and found to be the original compound unchanged.

Action of Acetic Anhydride and Sulphuric Acid on the Monocarboxylic Acid.

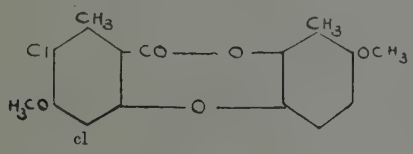


0·1 g. of monocarboxylic acid, m.p. 138–139° C., was dissolved in 6 c.c. acetic anhyride, a few drops of sulphuric acid were added, and the whole allowed to stand for two hours. It was then poured into 20 c.c. water, and after two hours the precipitate collected and crystallized from 20 c.c. hot ligroin. A substance, m.p. 208–209° C., was obtained.

4·355 mg. dried at 100° C in vac. No loss.
4·355 mg. gave 8·850 mg. CO_2; 1·420 mg. H_2O.
5·457 mg. gave 4·160 mg. AgCl.
3·890 mg. gave 5·280 mg. AgI.

Found: C = 55·4; H = 3·62; Cl. = 18·7; OCH_3 = 17·8.
$C_{15}H_9O_3Cl_2(OCH_3)_3$ requires C = 55·28; H = 3·79; Cl = 19·2; OCH_3 = 16·8.

Action of Methyl Alcoholic Potash on Compound.



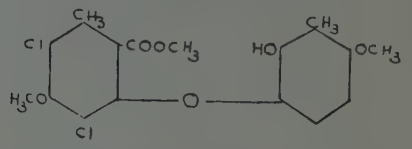
0·05 g. of compound, m.p. 208–209° C., suspended in 1 c.c. methyl alcohol was heated under a reflux with 5 c.c. of 5 % methyl alcoholic potash for one hour. On cooling, the solution was filtered and acidified. The white precipitate was collected and crystallized from ligroin and gave a material, m.p. 164° C.

No loss in weight when dried in vacuo at 100° C.
3·353 mg. gave 6·650 mg. CO_2 and 1·350 mg. H_2O.
5·137 mg. gave 4·060 mg. AgCl.
5·048 mg. gave 8·510 mg. AgI.

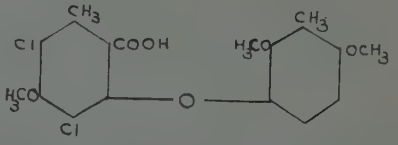
Found: C = 54·09; H = 4·4; Cl = 19·5; OCH_3 = 22·2.
$C_{15}H_9O_3Cl_2(OCH_3)_3$ requires C = 53·9; H = 4·5; Cl = 17·7; OCH_3 = 23·2.

The product gives no colour with either ferric chloride or bleaching powder, but it gives a bright blue indophenol reaction.

Methylation of Compound.

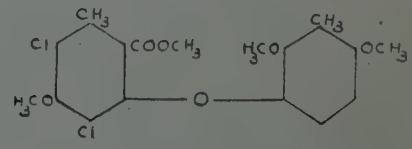


The substance, m.p. 164° C., did not methylate readily with diazomethane. 0·3 g. of the compound was dissolved in 30 c.c. dry acetone and boiled for 1½ hours with 2 c.c. dimethyl sulphate and 4 g. anhydrous potassium carbonate. Then 0·5 c.c. dimethyl sulphate and 2 g. potassium carbonate were added, and heating continued for a further hour. On cooling, the solution was filtered from the potassium carbonate and allowed to evaporate to dryness, with a final drying over potassium hydroxide in a vacuum desiccator. The residue was then taken up in ether, and extracted with a 1 per cent. solution of sodium hydroxide. The ether layer was washed with acid and finally with water before drying. The ether was evaporated off, and steam blown through the residual oil to remove the excess dimethyl sulphate. The residue was taken up in ether, washed, dried, and the solvent evaporated leaving a light yellow gum, which crystallized readily from methyl alcohol to give a substance, m.p. 78–79° C. On admixture with the compound formed by direct action of diazomethane on the mono-carboxylic acid,



there was no depression in melting point. The ester gives no reaction with either bleaching powder, ferric chloride, or 2 : 6 dichlor quinone chlorimide.

Action of Chlorine followed by Reduction on Compound.



0·08 g. of the compound, m.p. 78–79° C., was dissolved in 10 c.c. chloroform, and to the solution was added 5 c.c. of a solution of chlorine in carbon tetrachloride containing 0·04 g. Cl per c.c. After standing overnight the solution was poured into a beaker and evaporated, leaving a brown gum which did not crystallise from methyl alcohol, ligroin, or 40/60 petrol. The

gum was dissolved in 3 c.c. acetic acid, and to this was added a solution of 0·3 g. stannous chloride in 3 c.c. of 20 per cent. hydrochloric acid. The oil lightened in colour to yellow, and on dilution with water a yellow oil was precipitated (A). On further dilution of the decanted mother liquors and long standing, a small amount of white needles separated, which had a melting point less than 100° C. These crystals were soluble in sodium hydroxide without colour change; they gave a violet colour with ferric chloride, and no reaction with bleaching powder.

The oil (A) was dissolved in 5 c.c. of 10 per cent. methyl alcoholic potash; the solution after filtration was heated for 1 hour in a hydrogen atmosphere, after which time it was diluted with twice its volume of water, and acidified. The precipitate was taken up in ether, and extracted with sodium bicarbonate, which gave a small amount of crystals giving a port colour with ferric chloride. The ethereal solution was then extracted with 1 per cent. sodium hydroxide, yielding a substance which, after washing with ligroin, was crystallized from dilute methyl alcohol, and gave a compound, m.p. 77–77·5° C. This compound gave a purple ferric chloride reaction, no bleaching powder reaction, and a violet purple indophenol reaction.

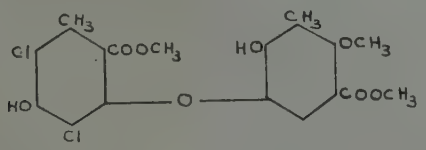
3·657 mg. gave 6·100 mg. CO_2; 1·230 mg. H_2O.
3·569 mg. gave 6·200 mg. AGI.
3·670 mg. gave 3·900 mg. AgCl.
0·632 mg. in 6·368 mg. camphor gave D 14·8°.

Found: C = 45·49; H = 3·74; Cl = 26·3; OCH_3 = 22·9.
$C_{10}H_{10}O_4Cl_2$ requires C = 45·28; H = 3·77; Cl = 26·8; OCH_3 = 23·4.

Found: M.W. = 268 required = 265.

On admixture with 5 methoxy 4·6 dichlor o-orsellinic methyl ester, m.p. 79–80° C., the mixed melting point showed no depression.

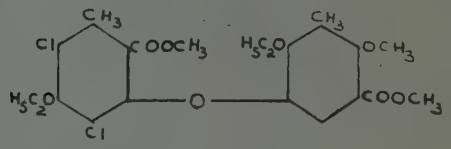
Ethylation of Gangaleoidin Methyl Ester.



0·4 g. of gangaleoidin methyl ester in 20 c.c. acetone was ethylated with an ethereal solution of diazoethane (from 8 c.c. nitroso-n-ethyl urethane). After standing overnight the solvents were evaporated, and the residue crystallized from hot ligroin. Crystals were obtained, m.p. 155° C.

4·542 mg. gave 10·670 mg. AgI = 31·0% OCH_3.
$C_{16}H_7O_3Cl_2(OCH_3)_3(OC_2H_5)_2$ requires 30·9% OCH_3.

Hydrolysis of the Ethylated Compound.

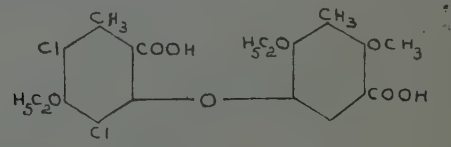


0·8 g. of compound was heated for 14 hours under reflux with 80 c.c. of 15 per cent. methyl alcoholic potash, after which time a sample on dilution with water showed no turbidity. After evaporating off the alcohol in an air draught the residue was diluted with 200 c.c. water, and acidified. The precipitate, after standing overnight, was collected and crystallized from 50 per cent. aqueous alcohol, and gave a substance, m.p. 215° C.

4·100 mg. gave 8·100 mg. CO_2 and 1·710 mg. H_2O.
4·907 mg. gave 3·170 mg. AgCl.
4·082 mg. gave 6·420 mg. AgI.

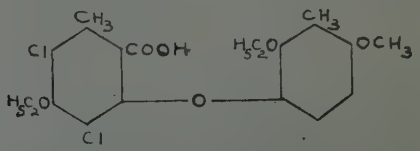
Found: C = 53·88; H = 4·6; Cl = 16·0; OCH_3 = 20·8.
$C_{14}H_7OCl_2(COOH)_2(OCH_3)(OC_2H_5)_2$ requires C = 53·3;
H = 4·65; Cl = 15·0; OCH_3 = 19·6.

Decarboxylation with Formic Acid of Compound.



1·0 g. was heated to boiling under reflux with 10 c.c. 98–100 per cent. formic acid for half an hour. After cooling, the solution was diluted with 40 c.c. water, and the precipitate allowed to stand overnight. It was collected, and gave a product, m.p. 161–163° C.

Methylation of Monocarboxylic Acid.



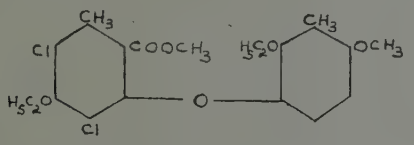
0·5 g. of the compound, m.p. 161–163° C., in 10 c.c. dry acetone was methylated with an ethereal solution of diazomethane (from 15 c.c. nitroso-N-methyl urethane), and allowed to stand overnight. On evaporation of the

solvents the residue was crystallized from warm methyl alcohol yielding a substance, m.p. 103–104° C.

3·623 mg. gave 7·480 mg. CO_2, 1·630 mg. H_2O.
5·132 mg. gave 3·360 mg. AgCl.
4·965 mg. gave 10·720 mg. AgI.

Found: C = 56·30; H = 5·0; Cl = 16·2; OCH_3 = 28·5.
$C_{14}H_8OCl_2(COOCH_3)(OC_2H_5)_2(OCH_3)$ requires C = 56·88;
H = 5·46; Cl = 16·0; OCH_3 = 28.

Action of Chlorine followed by Reduction on the Compound.



To a solution of 0·6 g. of compound, m.p. 103–104° C., in chloroform was added 13·3 c.c. of chlorine in carbon tetrachloride which contained 0·04 g. chlorine per c.c. After standing overnight the excess chlorine was removed by blowing dry air through the solution, and the solvents removed by evaporation. The residue was a greenish oil. This oil was reduced in acetic acid solution (30 c.c.) with 2 g. stannous chloride in 60 c.c. of 20 per cent. hydrochloric acid. The colour lightened, and on standing an oily material was precipitated. The mother liquors were decanted, and the solid washed with a little 5 per cent. hydrochloric acid and then with water. The oil was then boiled with 30 c.c. of 10 per cent. methyl alcoholic potash under reflux for one hour. After filtering off sodium chloride and diluting with twice its own volume of water the solution was acidified, and the precipitate extracted with ether. The ethereal solution was extracted with 3 per cent. sodium bicarbonate and then 1 per cent. sodium hydroxide. After acidifying the hydroxide layer, the white precipitate was taken up in ether, washed, dried, and the ether evaporated. The solid recovered was crystallized from dilute methyl alcohol, and a substance, m.p. 88–89° C., was obtained.

3·910 mg. gave 6·780 mg. CO_2 and 1·570 mg. H_2O.
4·958 mg. gave 5·160 mg. AgCl.
4·853 mg. gave 7·940 mg. AgI.

Found: C = 47·3; H = 4·46; Cl = 25·7; OCH_3 = 21·6.
$C_7H_4OCl_2(OC_2H_5)(COOCH_3)$ requires C = 47·3; H = 4·3;
Cl = 25·4; OCH_3 = 22·2.

Action of Chlorine followed by Reduction on Gangaleoidin Methyl Ester.

7 g. of the compound were dissolved in 200 c.c. chloroform, and to the solution was added 115 c.c. of a solution of chlorine in carbon tetrachloride (1 c.c. of solution contained 0·04 g. chlorine per c.c.); the whole, being tightly stoppered, was left overnight. Air was bubbled through the solution to remove the excess chlorine, and then the solvents were distilled off under reduced pressure, leaving a dark brown gum. The gum was reduced in acetic acid solution (175 c.c.) by 12 g. stannous chloride in 360 c.c. of 20 per cent. hydrochloric acid. The colour lightened to yellow and solid separated on dilution.

After standing overnight the liquors were decanted from a gum. The gum was taken up in ether, and extracted successively with 3 per cent. sodium bicarbonate, 3 per cent. sodium carbonate, and 3 per cent. sodium hydroxide. The decantate was extracted with chloroform, and the extract recovered from the chloroform. On distillation with superheated steam, the chloroform extract, the sodium bicarbonate, and sodium hydroxide extracts all yielded the same substance, m.p. 114–115° C., which on admixture with 4·6 dichlor o-orsellinic methyl ester showed no depression in melting point. The sodium carbonate extract was recovered and washed with cold benzene, leaving behind a substance, m.p. 114–115° C., which was 4·6 dichlor o-orsellinic methyl ester.

4·608 mg. gave 4·260 mg. AgI.
2·582 mg. gave 2·820 mg. AgCl.

Found: OCH_3 = 12·15; Cl = 27·0.
$C_7H_5O_2Cl_2(COOCH_3) . \frac{1}{2}H_2O$ requires OCH_3 = 11·9; Cl = 27·3.

The benzene solution on evaporation gave a residue which on crystallization from benzene gave crystals, m.p. 156° C., which was the monochlor derivative of gangaleoidin methyl ester.

4·007 mg. gave 6·890 mg. CO_2 and 1·300 mg. H_2O.
4·790 mg. gave 4·430 mg. AgCl.
4·775 mg. gave 7·200 mg. AgI.

Found: C = 46·9; H = 3·6; Cl = 22·9; – OCH_3 = 19·9.
$C_{16}H_8O_5Cl_2(OCH_3)_3$ requires C = 47·5; H = 3·5; Cl = 22·2; – OCH_3 = 19·4.

The compound gives a negative ferric chloride reaction, a yellow colour with bleaching powder, and a slate-grey colour with 2 : 6 dichlor quinone chlorimide.

Methylation of the Monochlor-derivative of Gangaleoidin Methyl Ester, m.p. 156° C.

1·0 g. of the compound in acetone solution was methylated with an ethereal solution of diazomethane (10 c.c. nitroso-N-methyl urethane). After standing

for 22 hours the solvents were evaporated to a greenish oil, which crystallized from methyl alcohol, m.p. 98–100° C.

5·948 mg. gave 13·820 mg. AgI.

Found: OCH_3 = 30·6.
$C_{16}H_6O_3Cl_3(OCH_3)_5$ requires = 30·5.

0·9 g. of the compound, m.p. 98–100° C., was boiled for 5 hours with 63 c.c. of 15 per cent. methyl alcoholic potash. The solution was evaporated to dryness in air. The solid residue was dissolved on 45 c.c. water, acidified to 5 per cent. alkalinity, and filtered. The filtrate was then made acid, and extracted with ether. A brown gum was obtained on evaporating the solvent, which crystallized from aqueous methyl alcohol, and gave a product, m.p. 227–228° C.

3·931 mg. gave 6·620 mg. CO_2 and 1·410 mg. H_2O.
4·718 mg. gave 4·000 mg. AgCl.
4·098 mg. gave 5·750 mg. AgI.

Found: C = 45·9; H = 3·98; Cl = 21·1; OCH_3 = 18·5.
$C_{16}H_8O_5Cl_3(OCH_3)_3 . H_2O$ requires C = 45·8; H = 3·8; Cl = 21·4; OCH_3 = 18·7.

Attempted Decarboxylation of the above Dicarboxylic Acid, m.p. 227–8° C.

0·44 g. compound was boiled with 15 c.c. of 98 per cent. formic acid for 30 minutes. The solution was then cooled and diluted. After standing for two hours the precipitate was collected, m.p. 222° C. It was the unchanged dicarboxylic acid, and was methylated back to the compound, m.p. 98–100° C., referred to above, with diazomethane.

Vacuum Distillation of Gangaleoidin Methyl Ester, m.p. 197° C.

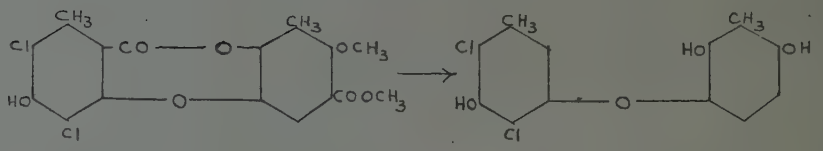
2 g. were distilled under reduced pressure in four portions of 0·5 g. each. The distillate, a red oil, was washed with 8 c.c. warm ligroin, and the solvent decanted. To the decantate was added 2 c.c. benzene, and the solution left overnight, when it was again decanted from some oily solid. The residue, obtained by evaporating the decantate, was crystallized from 50 per cent. aqueous methyl alcohol, and had a melting point 112–113° C., which was not depressed on admixture with a sample of 4 : 6 dichlor o-orsellinic methyl ester. The red oil insoluble in warm ligroin was dissolved in 4 c.c. benzene, and after some oil had separated on standing, the solution was decanted. After some time a white globular solid was precipitated, which was washed with a few drops of alcohol. The product was finally crystallized from a mixture of 1 c.c. benzene and 1 c.c. ligroin, and yielded a product, m.p. 180–181° C., which on admixture with the original material melted at 166° C. The compound gave a

blue quinone chlorimide reaction, whereas the original material yields a steel colour.

4·717 mg. gave 8·825 mg. CO_2; 1·690 mg. H_2O.
3·488 mg. gave 5·330 mg. AgI.
8·669 mg. gave 5·490 mg. AgCl.
0·281 mg. in 4·007 mg. camphor gave 5·6° D.
0·270 mg. in 6·059 mg. camphor gave 3·5° D.

Found: C = 51·03; H = 3·98; Cl = 15·7; OCH_3 = 20·2; MW = 501; 509.
$C_{16}H_9O_5Cl_2(OCH_3)_3$ requires C = 51·24; H = 4·04; Cl = 16·0;
OCH_3 = 20·9; MW = 445.

Demethylation of Gangaleoidin.



0·5 g. gangaleoidin in 10 c.c. glacial acetic acid was heated with 1 g. red phosphorus and 8 c.c. constant boiling hydrobromic acid (b.p. 126° C; 47·8 per cent.) for six hours under a reflux. After cooling, the whole was diluted with 100 c.c. of water and saturated with sodium bisulphite to decolourize. When the mixture had stood overnight it was filtered. From the filtrate was recovered by ether extraction a product which was a yellow oil and showed no inclination to crystallize. During treatment with steam a change appeared to occur as the product gradually went into solution in the hot water, from which it crystallized in small granular plates, m.p. 111–112° C. It was soluble in 3 per cent. sodium carbonate solution, and contained halogen. The compound gave no colour with ferric chloride, a blood-red colour with bleaching powder, and a dark pink with 2 : 6 dichlor quinone chlorimide.

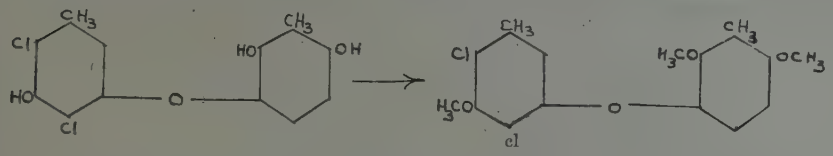
4·278 mg. dried at 50° C. showed no loss.

When the compound is dried at 100° C. in vacuo complete sublimation occurs.

4·278 mg. gave 7·900 mg. CO_2; 1·670 mg. H_2O.
5·030 mg. gave 4·230 mg. AgCl.
Methoxyl negative.

Found: C = 50·36; H = 4·3; Cl = 20·8.
$C_{14}H_{12}O_4Cl_2 \cdot H_2O$ requires C = 50·4; H = 4·2; Cl = 21·3.

Methylation of Product Obtained in the Demethylation of Gangaleoidin.



0·1 g. of the demethylated compound was dissolved in 5 c.c. of 3·5 N caustic soda, and shaken with 1·5 c.c. dimethyl sulphate for 30 minutes, after which time a solid separated. The reaction was finished by heating the whole on a boiling water bath. The solid was collected, crystallized from 60/80 petrol ether, and washed with methyl alcohol, when a product, m.p. 108–109° C. was obtained. A mixed melt with the methyl ether of the phenolic body obtained by heating the dicarboxylic acid, m.p. 216° C., in glycerine (Nolan and Keane, *loc. cit.*) showed no depression.

3·901 mg. gave 8·240 mg. CO_2; 1·800 mg. H_2O.
4·264 mg. gave 8·140 mg. AgI.

Found: C = 57·6; H = 5·12; OCH_3 = 25·2.
$C_{14}H_9OCl_2(OCH_3)_3$ requires C = 57·14; H = 5·04; OCH_3 = 26·1.

Acidification of the alkaline liquors from this methylation gave a solid which on crystallization from aqueous methyl alcohol had m.p. 165–166° C., and was identical with the phenolic body obtained by heating the dicarboxylic acid, m.p. 216° C., in glycerine (Nolan and Keane, *loc. cit.*). The product gives a blue indophenol reaction identical with that obtained with the phenolic body; neither the product obtained here nor the phenolic body gave a colour with bleaching powder or ferric chloride.

Potash Fusion of Gangaleoidin Methyl Ester.

20 g. potassium hydroxide pellets and 2 c.c. water were warmed to 100° C. in a nickel crucible. (A thermometer with the bulb encased in a brass sleeve served to read the temperature and acted as a stirrer.) 1 g. gangaleoidin methyl ester was added to the melt, and the temperature was raised gradually to 250° C., where it was maintained for 20 minutes. A further period of 5 minutes at 310° C. completed the fusion. The mass was then allowed to cool, was dissolved in 100 c.c. water, and the solution saturated with carbon dioxide. After acidification with dilute sulphuric acid the solution was extracted with ether. The brown gum obtained on evaporating the solvent was boiled in water with norite, and filtered. From the solution, large colourless crystals separated, which decomposed at 263° C. with previous browning. The product gave a blood-red bleaching powder reaction, but no coloration with ferric chloride. It contains no methoxyl.

C–CH_3 determinations.

12·220 mg. – 2·58 c.c. N/100 NaOH.
8·128 mg. – 1·10 c.c. N/100 NaOH.
3·637 mg. gave 7·270 mg. CO_2 and 1·690 mg. H_2O.
3·502 mg. in vacuo @ 110° C. lost 0·315 mg.
2·988 mg. in vacuo @ 110° C. lost 0·260 mg.
4·005 mg. in vacuo @ 105° C. lost 0·405 mg.

Found: C = 54·5; H = 5·1; C–CH_3 = 3·16, 2·02; H_2O = 8·99, 8·72, 10·1.
$C_{14}H_{12}O_6 1\frac{3}{4}H_2O$ requires C = 54·63; H = 5·04; C–CH_3 = 4·88; H_2O = 10·4.

3·565 mg. (vac. dried) gave 7·900 mg. CO_2 and 1·490 mg. H_2O.

Found: C = 60·4; H = 4·3.
$C_{14}H_{12}O_6$ requires C = 60·87; H = 4·35.

Acetylation of the Fusion Product.

0·05 g. of the compound was dissolved in 3 c.c. acetic anhydride and 1 drop of sulphuric acid, and allowed to stand for two hours. The solution was then poured on to 10 g. crushed ice, and allowed to stand overnight, when crystals, m.p. 178–179° C., separated, which were crystallized from benzene. The crystals were easily soluble in sodium carbonate.

3·598 mg. gave 7·780 mg. CO_2 and 1·410 mg. H_2O.
3·908 mg. gave 8·500 mg. CO_2 and 1·610 mg. H_2O.
7·881 mg. – 7·19 c.c. N/100 NaOH.
0·627 mg. in 5·723 camphor gave 10·2 D.

Found: C = 59·1; 59·3. H = 4·3; 4·5. CH_3CO = 39·2. M.W. = 398.
$C_{14}H_8O_6(CH_3CO)_4$ requires C = 59·46; H = 4·55; CH_3CO = 38·74; M.W. = 444.

Methylation of the above Acetyl Derivative.

0·1 g. of the acetyl derivative was methylated in acetone solution with an ethereal solution of diazomethane (4 c.c. nitroso-N-methyl urethane). After 20 hours the solvents were evaporated, and the solid crystallized from methyl alcohol, m.p. 109–110° C.

3·584 mg. gave 7·920 mg. CO_2 and 1·570 mg. H_2O.
3·779 mg. gave 8·210 mg. CO_2 and 1·700 mg. H_2O.
3·690 mg. gave 2·050 mg. AgI.
4·110 mg. gave 2·240 mg. AgI.
8·020 mg. – 7·36 c.c. N/100 NaOH.

Found: C = 60·27; 59·60. H = 4·87; 5·03. OCH_3 = 7·37; 7·25. CH_3CO = 39·4.
$C_{14}H_7O_5(OCH_3)(CH_3CO)_4$ requires C = 60·26; H = 4·8; OCH_3 = 6·77; CH_3CO = 37·55.

Methylation of the Fusion Product.

0·1 g. of the compound was dissolved in 2·2 c.c. of 2N. NaOH. To this solution were added three separate lots of 0·12 c.c. dimethyl sulphate, shaking vigorously after each addition. Finally, 0·6 c.c. of 2 N. NaOH was added, and the whole heated under a reflux condenser on a boiling water bath for half an hour. After acidification the ether extract was evaporated to a solid, which crystallized from methyl alcohol, m.p. 178° C.

3·580 mg. gave 8·570 mg. CO_2 and 2·000 mg. H_2O.
3·784 mg. gave 10·040 mg. AgI.
0·737 mg. in 6·670 mg. camphor gave 11·8° D.

Found: C = 65·2; H = 5·9; OCH_3 = 35·0; M.W. = 346.
$C_{14}H_8O_2(OCH_3)_4$ requires C = 65·06; H = 6·02; OCH_3 = 37·35; M.W. = 332.

Potash Fusion of 4·6 Dichlor O-Orsellinic Methyl Ester, m.p. 113° C.

20 g. potassium hydroxide pellets and 2 c.c. water were warmed to 100° C. in a nickel crucible. 0·9 g. compound was added to the melt, and the temperature was raised gradually to 250° C., where it was maintained for 20 minutes. A further period of 5 minutes at 310° C. completed the fusion. The mass was then allowed to cool, was dissolved in 100 c.c. water, and the solution saturated with carbon dioxide. After acidification with dilute sulphuric acid the solution was extracted with ether. The brown gum obtained on evaporating the solvent was boiled in water with norite, and filtered. A white solid was obtained on concentrating the solution, which was crystallized from a mixture of acetic acid and benzene (1 : 2), m.p. 229–230° C. The product on admixture with a sample of α-resorcylic acid showed no depression in melting point.

Potash Fusion of Diploicin.

20 g. potassium hydroxide pellets and 2 c.c. water were warmed to 100° C. in a nickel crucible and 1 g. of diploicin was added. The temperature was carefully raised to 250° C., where it was maintained for 20 minutes. A further period of five minutes at 310° C. completed the fusion. When the melt had cooled, it was dissolved in 100 c.c. water, the solution saturated with carbon dioxide, acidified with dilute sulphuric acid, and extracted with ether. The ethereal solution on evaporation gave a good yield of oily crystals, which were clarified by boiling in aqueous solution with norite. The solid obtained on concentrating the aqueous liquors was crystallized from a mixture of acetic acid and benzene (1 : 2), yielding a product, m.p. 228–229° C., not depressed on admixture with α-resorcylic acid.

No. 16.

ATMOSPHERIC POLLUTION IN DUBLIN DURING THE YEAR 1942.

By A. G. G. LEONARD, BRIDGET P. McVERRY, and D. CROWLEY.

[Read May 25. Published separately September 20, 1943.]

Observations continued during 1942 conclude a period of five years at Leinster Lawn and of four years at the Albert Farm, Glasnevin.

Results obtained with Standard Gauges.

Detailed figures for deposits during 1942 are given for Leinster Lawn in Table 1 and for the Albert Farm in Table 2.

A partial summary of the results obtained from 1938 to 1942 is given in Table 3, in which deposits are given in metric tons per 100 sq. kilometres. It

RESULTS OBTAINED WITH DEPOSIT GAUGES, 1938–1942

	LEINSTER LAWN							ALBERT FARM						
YEAR	RAINFALL IN MMS.	INSOLUBLE SOLIDS	△	SOLUBLE SOLIDS	△	TOTAL SOLIDS	△	RAINFALL IN MMS.	INSOLUBLE SOLIDS	△	SOLUBLE SOLIDS	△	TOTAL SOLIDS	△
1938	697	3911		2737		6648		—	—		—		—	
1939	736	4223	312	2693	-44	6916	268	731	932		1620		2552	
1940	723	4505	282	2946	253	7451	535	695	1071	139	1648	28	2719	167
1941	705	5032	527	2980	34	8012	561	604	1473	402	1785	137	3258	539
1942	627	5260	228	2601	-379	7861	-151	637	1497	24	1584	-201	3081	-177

Table 3.

will be seen that there was a slight decline in both insoluble and soluble deposits during 1942, but if one examines the figures for total solids there is on the whole a decided upward trend from 1938 to 1942 at Leinster Lawn, and also at the Albert Farm from 1939 to 1942. The decline during 1942 is probably to be ascribed to the substitution of other fuels for coal.

TABLE 1.—*Impurity Deposited from the Atmosphere at Leinster Lawn during the Year 1942.*

Grams per square Decametre (Metric Tons per Hundred Square Kilometres).

	Rainfall. mm.	pH of rain-water.	*Insoluble Matter.*			*Soluble Matter.*		Total solids.	*Included in Soluble Matter.*			
			Tar.	Carbon-aceous other than tar.	Ash.	Loss on ignition.	Ash.		Sulphates (SO_3).	Chlorine (Cl).	Ammonia (NH_3).	Lime (CaO).
January	74	5·0	6	175	234	124	225	764	83	96	9	31
February	24	5·0	11	144	261	41	117	574	52	16	3	33
March	66	5·8	12	202	309	56	158	737	66	36	2	20
April	27	6·2	11	210	293	63	131	708	37	31	1	32
May	72	6·0	11	203	264	126	162	766	73	47	4	—*
June	4	6·8	7	209	198	20	60	494	21	5	—	14
July	48	6·4	7	198	189	36	132	562	40	15	—	35
August	86	6·1	11	243	258	103	194	809	80	26	—	28
September	101	5·8	11	162	193	74	137	577	54	46	1	25
October	39	5·6	11	171	214	61	127	584	51	25	3	27
November	11	5·2	6	190	225	67	129	617	68	8	6	26
December	75	5·8	5	136	270	92	166	669	56	60	8	32
Mean Monthly	52		9	187	242	72	145	655	57	34	3	28
Summer Total	338		58	1225	1395	422	816	3916	305	170	6	134
Winter Total	289		51	1018	1513	441	922	3945	376	241	32	169
Annual Total	627		109	2243	2908	863	1738	7861	681	411	38	303

* No estimation.

when pollution was somewhat high the deposits left on the filter paper were distinctly brownish in colour as contrasted with the black stains obtained in previous years when coal was available. This is obviously due to the substitution of peat for coal. On one day only, November 11th, was a "hazy" day recorded. It is interesting to note that on the evening of 5th January, 1943, when a dense fog occurred in parts of Dublin city, the maximum shades obtained on the automatic filter reached a value of 2, recorded at 5 and 6 p.m. and 10 and 11 p.m. The fog was evidently a "white" fog due to condensed moisture, and was not to be attributed directly to solid suspended particles. Such fogs occur when a stratum of warm and less dense air acts as a "lid," preventing the normal rise of moisture-laden air from the earth's surface. (24th Rep. A.P.R.C., 1938, p. 102.)

Suspended Impurity and Deaths from Respiratory Diseases.

Graphs of moving averages for each of these quantities are given in the lower part of fig. 3, and a similar graph for temperatures ° F. is given in the upper portion. The complete graphs extend over five years. It will be noted that periods of minimum temperature are also periods of maximum pollution, and that such periods are followed by periods of maxima in the deaths from respiratory diseases in Dublin city. From 1940 onwards there is a progressive decline in pollution due to suspended impurity and there is also a similar decline in the deaths.

January of the year 1940 shows the lowest temperature of the five years under consideration, it also gives the highest pollution and a remarkable peak in deaths. The following winters were years of coal shortage and consequent diminishing pollution by suspended impurity and sulphur dioxide, the two latter declining in January, 1942, and January, 1943, to values obtaining in the summers of preceding years. The deaths in January, 1942, and January, 1943, however, while the lowest during the five years under review, show well-marked maxima above the summer levels. Such maxima cannot be ascribed to atmospheric pollution, and must be due to other causes. If records were maintained over a sufficient period of years it might therefore be possible to make some differentiation between the increase of deaths in winter due to pollution and those due to other causes. It will be interesting to see how the figures are affected when coal is again available in normal suppy as domestic fuel.

Sulphur Dioxide.

Pollution due to sulphur dioxide at Leinster Lawn and Albert Farm was similar to but somewhat lower than in 1941 (fig. 2). As in previous years there is a distinct degree of parallelism between the curves for SO_3 and suspended impurity at Leinster Lawn.

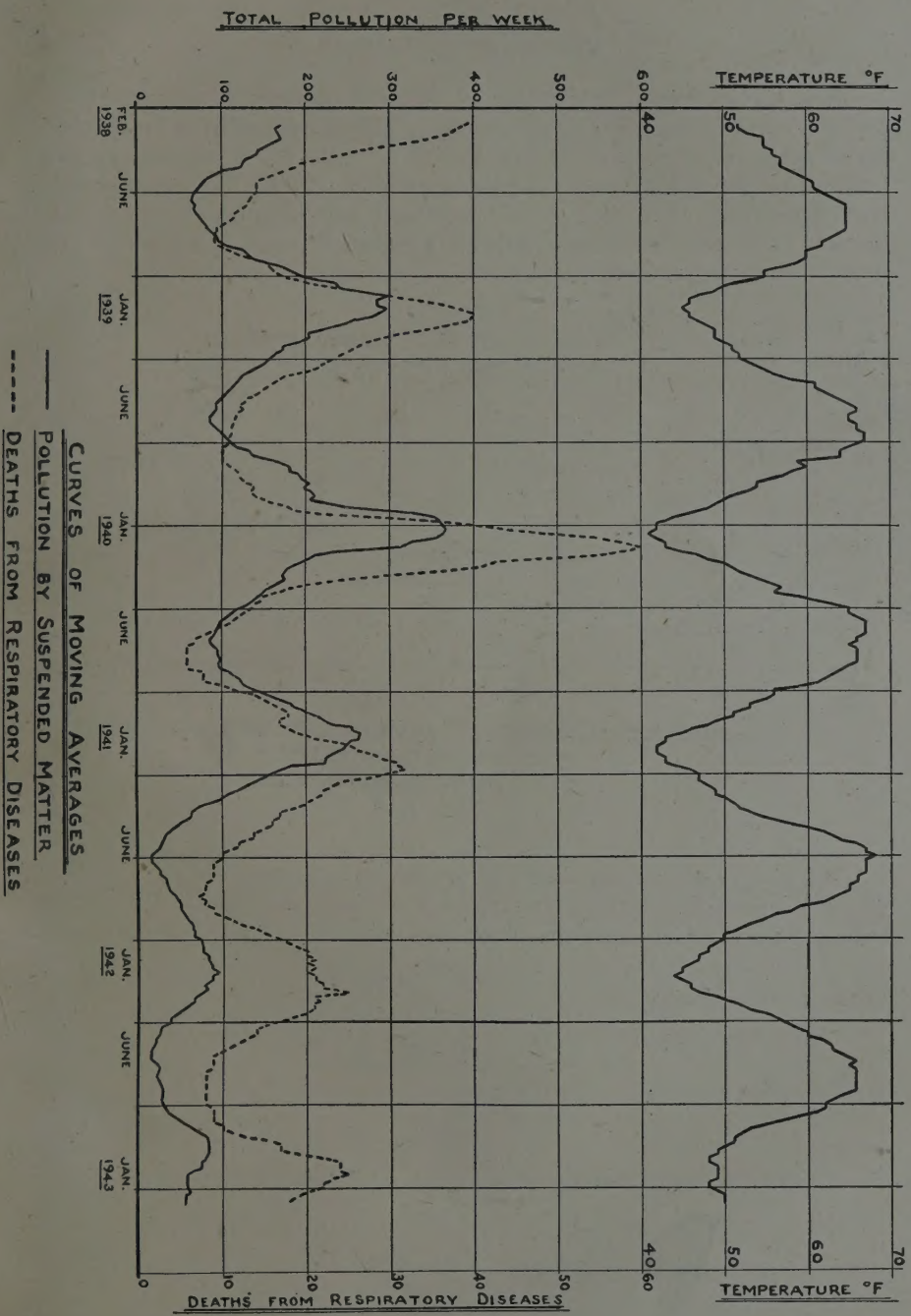

TOTAL POLLUTION PER WEEK
TEMPERATURE °F
0
100
200
300
400
500
600
40
50
60
70
FEB. 1938
JUNE
JAN. 1939
JUNE
JAN. 1940
JUNE
JAN. 1941
JUNE
JAN. 1942
JUNE
JAN. 1943
CURVES OF MOVING AVERAGES.
POLLUTION BY SUSPENDED MATTER.
DEATHS FROM RESPIRATORY DISEASES
0
10
20
30
40
50
60
DEATHS FROM RESPIRATORY DISEASES
TEMPERATURE °F

FIG. 3.

Measurement of Sunlight.

Fig. 4 gives results for liberation of iodine by sunlight at Merrion Street and the Albert Farm during two periods. The loss of sunlight at Merrion Street being 36 per cent. in the first and 24 per cent. in the second. In the previous corresponding periods the losses were only 26 per cent. and 15 per cent. respectively. In view of the continued low pollution by suspended impurity, this increase in loss of daylight at Merrion Street is unexpected.

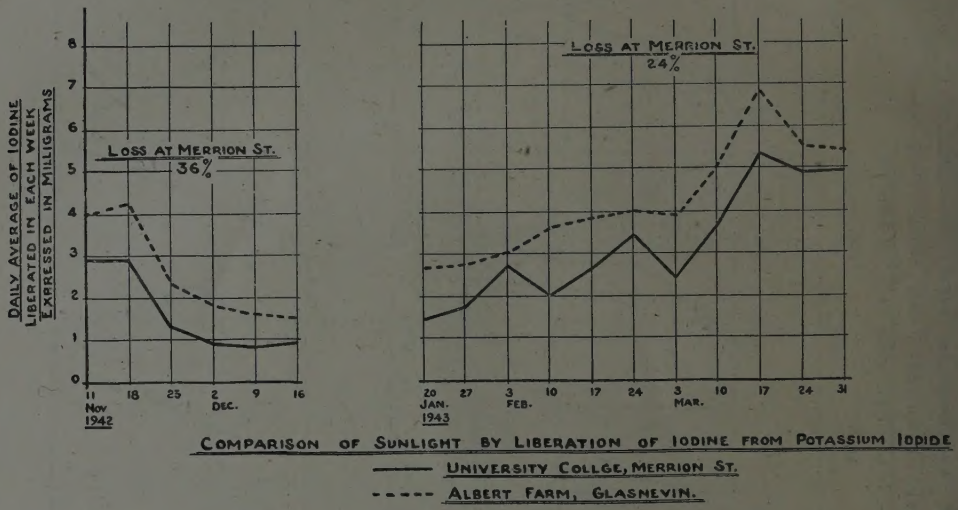


FIG. 4.

We wish to express our thanks to the Registrar-General and the Director of the Meteorological Service for supplying necessary data and to University College for a grant in aid of the analytical work.

CHEMICAL DEPARTMENT,

UNIVERSITY COLLEGE, DUBLIN.

SCIENTIFIC PROCEEDINGS.

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